



## Evaluation of platinum catalysts for naval submarine pollution control

Matthew J. Kale <sup>a,1</sup>, Dillon Gidcumb <sup>b,1</sup>, Franklin J. Gulian <sup>c</sup>, Steven P. Miller <sup>c</sup>, Christopher H. Clark <sup>d</sup>, Phillip Christopher <sup>a,b,e,\*</sup>

<sup>a</sup> Department of Chemical & Environmental Engineering, University of California, Riverside, 900 University Ave. Riverside, CA 92521, United States

<sup>b</sup> Program in Materials Science & Engineering, University of California, Riverside, 900 University Ave. Riverside, CA 92521, United States

<sup>c</sup> Naval Surface Warfare Center (NSWC), Philadelphia Division, 5001 S. Broad St. Philadelphia, PA 19112, United States

<sup>d</sup> Naval Surface Warfare Center (NSWC), Corona Division, 1999 4th St. Norco, CA 92860, United States

<sup>e</sup> UCR Center for Catalysis, University of California, Riverside, 900 University Ave. Riverside, CA 92521, United States



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### ABSTRACT

Catalytic air purification systems are required to maintain desirable levels of contaminants in confined space pollution control applications, such as onboard naval submarines. These systems execute oxygen generation, CO<sub>2</sub> removal, and burning of contaminants such as carbon monoxide (CO), and hydrocarbons. Crucial characteristics of the catalytic burners on submarines include high activity toward CO combustion, long-term stability in humid environments, and minimal activity towards the decomposition of trace halogenated compounds (often used as refrigerants) that can form toxic acid gas compounds. Here, we compare currently used hopcalite/LiOH catalysts to platinum (Pt) based catalysts deposited on Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> supports for CO combustion, tolerance to humid environments and combustion of model refrigerant contaminant molecules, freon 134a and methyl chloride. The three catalysts exhibit complete combustion of CO in dry air streams by 110 °C, and no catalyst was found to activate freon 134a up to 400 °C. Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> catalysts outperformed hopcalite/LiOH by showing enhanced CO oxidation reactivity in the presence of humidity (hopcalite/LiOH is strongly deactivated when H<sub>2</sub>O is co-fed), and they are minimally active towards methyl chloride oxidation up to 275 °C, whereas hopcalite/LiOH is active below 200 °C. Pt/CeO<sub>2</sub> exhibited higher reactivity for CO oxidation and lower activity for methyl chloride oxidation, as compared to Pt/Al<sub>2</sub>O<sub>3</sub>. The results strongly suggest that Pt based catalysts, similar to those used in automotive catalysis, may be excellent replacements for currently utilized hopcalite/LiOH catalysts in naval submarine pollution control applications.

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### 1. Introduction

Heterogeneous catalysts play a critical role in pollution control applications such as automotive catalytic converters, and the removal of contaminants in confined spaces [1]. Confined space pollution control is a critical component of life support systems on board closed-system manned vessels such as submarines, spacecraft, and mining operations [2,3]. These pollution control systems execute oxygen generation, CO<sub>2</sub> removal, and contaminant combustion, such as carbon monoxide (CO), hydrogen (H<sub>2</sub>) and hydrocarbons, as they are generated [4]. On submarines, the air

quality must be continuously maintained within safety standards by the constant removal of trace contaminants to enable extended dive times. Poor air quality control and the resulting necessity to vent the atmosphere can negatively impact tactical advantage in long-term missions.

One of the main air contaminants on board nuclear submarines that must be removed by active confined space pollution control systems is CO [4]. A common catalyst used in pollution control units (CO/H<sub>2</sub> burners) on board nuclear submarines is hopcalite, which is a mixture of copper oxide and manganese dioxide, (CuMn<sub>2</sub>O<sub>4</sub>, typically ~60% manganese dioxide, and 15–40% copper oxide) [5]. This catalyst has been used for the removal of CO in gas streams over the last century, and has been well characterized [6–12]. Hopcalite catalysts are active for CO removal from room temperature up to 400 °C, but dry gas streams must be used due to the well-known deactivation of hopcalite catalysts in the presence of humidity [12–17]. Higher operating temperatures must be used if humidity is present in the feed stream, which can increase operating

\* Corresponding author at: Department of Chemical & Environmental Engineering, University of California, Riverside, 900 University Ave. Riverside, California 92521, United States.

E-mail address: [christopher@engr.ucr.edu](mailto:christopher@engr.ucr.edu) (P. Christopher).

<sup>1</sup> These authors contributed equally to this work.

costs, result in decreased catalyst lifetimes, and drive the activation of halogenated air contaminant compounds, which are typically used as refrigerants [14]. Trace amounts of hydrochlorofluorocarbons (HCFCs) such as Freon 134a (1,1,1,2-tetrafluoroethane; freon herein) and methyl chloride ( $\text{CH}_3\text{Cl}$ ;  $\text{MeCl}$  herein) can be present in submarine atmospheres, due to the use of refrigerants, at concentrations below harmful levels. However, when circulated through catalytic  $\text{CO}/\text{H}_2$  burners with the ship air at elevated temperatures, these HCFCs can combust to form dangerous acid gases, such as phosgene and hydrofluoric acid, as was observed in the first patrol of the nuclear submarine USS Tecumseh [2]. To address this problem, adsorbent materials such as  $\text{LiOH}$  are used to remove the produced toxic acid gases, and prevent further contamination of the atmosphere. The requirement of  $\text{LiOH}$  adsorbent units to remove acid gases produced from HCFC combustion increases the pollution control system space utilization, which is undesired.

Ideal characteristics of the catalytic combustion systems for confined space pollution control on board submarines include high activity towards  $\text{CO}$ ,  $\text{H}_2$ , and hydrocarbon oxidation, long-term stability in humid environments, and no activity towards HCFC oxidation under typical operating conditions. It is clear from many years of work in automotive catalysis that precious metal catalysts provide excellent reactivity, thermal stability, and poison tolerance for  $\text{CO}$  and hydrocarbon oxidation under a wide range of operating conditions [17–19]. An important active component of automotive catalysis, dispersed Platinum (Pt) nanoparticles on oxide supports, also show promise for low temperature  $\text{CO}$  oxidation with high tolerance to humid environments [20–24]. However, there have been few comparative studies of Pt-based and hopcalite catalysts for confined space Naval pollution control applications [16,17,19], and none explore the impact of humidity, fluorinated and chlorinated hydrocarbons and metal oxide support composition.

Here, we compare hopcalite/ $\text{LiOH}$  catalysts with Pt-based catalysts supported on  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  supports for combustion of  $\text{CO}$  in dry and humid air streams, and oxidation reactivity towards model HCFC compounds (Freon 134a and  $\text{MeCl}$ ). Pt-based catalysts exhibited better performance for confined space pollution control systems in almost all metrics, as compared to hopcalite/ $\text{LiOH}$ . Pt-based catalysts exhibit complete  $\text{CO}$  removal above  $\sim 100^\circ\text{C}$ , no activity for freon activation up to  $400^\circ\text{C}$ , strong water tolerance, and minimal  $\text{MeCl}$  activation until  $>300^\circ\text{C}$ . Furthermore, the  $\text{CeO}_2$  supported Pt uniquely promotes  $\text{CO}$  oxidation rates at lower temperatures than  $\text{Al}_2\text{O}_3$  supported Pt, but remains more passive for  $\text{MeCl}$  oxidation at higher temperatures compared to  $\text{Al}_2\text{O}_3$  supported Pt. The results strongly suggest that automotive type catalysts that exploit Pt deposited on dispersed  $\text{CeO}_2$  on thermally stable  $\text{Al}_2\text{O}_3$  supports may be an excellent replacement for currently utilized hopcalite/ $\text{LiOH}$  catalysts in confined space pollution control applications.

## 2. Methods

### 2.1. Catalyst synthesis

Colloidal Pt particles were synthesized following an adapted procedure as described previously [25]. In a round bottom flask, 0.25 mL hexachloroplatinic acid solution (Sigma Aldrich, 8 wt.% in  $\text{H}_2\text{O}$ , 0.205 M) and 0.2298 g polyvinylpyrrolidone (PVP; Sigma Aldrich, 55,000 g/mol) was mixed with 5.0 mL of ethanol and 5.0 mL of deionized water. The solution was heated to  $100^\circ\text{C}$  and refluxed for 3 h while stirring at 1000 RPM. After cooling to room temperature, the Pt ink solution was prepared for slurry impregnation onto  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{CeO}_2$  supports at a weight loading of 0.5% Pt ( $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{CeO}_2$  henceforth). The pH of the ink solution was adjusted to 6 using a 0.05 M  $\text{NaOH}$ , and the appropriate amount of support

material ( $\sim 2.0\text{ g}$  of total catalyst) was added to the Pt nanoparticle solution and stirred for 14 h in ambient conditions. The solution was washed via centrifugation once with a 0.1 M  $\text{NH}_4\text{NO}_3$  solution and three times with deionized  $\text{H}_2\text{O}$ . The resulting catalyst was transferred to an evaporation dish to dry overnight in a vacuum oven ( $100\text{--}110^\circ\text{C}$ ). After drying, the samples were sieved (120 mesh) and calcined ( $500^\circ\text{C}$ ) for 5 h. Carulite 300 (hopcalite with no  $\text{LiOH}$ ), and hopcalite/ $\text{LiOH}$  (Carus Corporation) were used as received. In this report,  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  supports were chosen for direct comparisons with the supports used in monolithic catalytic converters.  $\text{Al}_2\text{O}_3$  was chosen because it is known to be thermally stable under harsh conditions and to bond reasonably strongly with Pt and therefore maintain a high degree of dispersion.  $\text{CeO}_2$  was chosen as it is known to significantly enhance the oxidation reactivity of Pt. These are both common supports used in the automotive industry for related catalytic reactions.

### 2.2. Reactor studies

Experiments were conducted in a temperature controlled quartz packed bed reactor, where the effluent gas concentrations were measured with online mass spectrometry (HALO 201, Hiden Analytical Inc.). Catalysts were sieved to  $<75\text{ }\mu\text{m}$  and diluted 10:1 with inert silica gel (Sigma Aldrich, high purity grade 150 Å) in order to prevent the influence of local heating and internal or external mass transfer limitations during low temperature experiments ( $<150^\circ\text{C}$ ) [26,27]. 50 mg of  $\text{Pt}/\text{CeO}_2$  and  $\text{Pt}/\text{Al}_2\text{O}_3$  and 100 mg of hopcalite/ $\text{LiOH}$  were used in all experiments. In this report, a larger mass of hopcalite/ $\text{LiOH}$  catalyst was utilized to account for strong deactivation observed in the presence of water in the reactant stream.

$\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{CeO}_2$  catalysts were pretreated *in-situ* by heating to  $230^\circ\text{C}$  and reducing in  $\text{H}_2$  (99.999%, Airgas) for 60 min. The reactor was flushed with He (99.999%, Airgas) and cooled to  $200^\circ\text{C}$ , where the catalyst was exposed to  $\text{CO}$  oxidation reaction conditions (100 ppm  $\text{CO}$ , 20%  $\text{O}_2$ , 10% Ar and balance He) for 6 h. The Pt catalysts were then cooled to  $30^\circ\text{C}$ , where a temperature ramp from  $30^\circ\text{C}$  to  $150^\circ\text{C}$ , holding every  $10^\circ\text{C}$  30 min, was performed to verify that the catalytic activity was consistent with previous measurements. Hopcalite/ $\text{LiOH}$  samples were heated to  $230^\circ\text{C}$  and calcined *in-situ* in  $\text{O}_2$  (99.999%, Airgas) for 60 min [10]. The reactor was flushed with He, cooled to  $200^\circ\text{C}$ , and exposed to reaction conditions. All further experiments with  $\text{H}_2\text{O}$ , Freon, and  $\text{MeCl}$  contaminants were performed using identical protocols.

For the exposure and low temperature ( $<150^\circ\text{C}$ )  $\text{CO}$  oxidation experiments performed in a humid environment, the temperature at which each catalyst exhibited  $\sim 30\text{--}80\%$  conversion (hopcalite/ $\text{LiOH}$  =  $50^\circ\text{C}$ ,  $\text{Pt}/\text{CeO}_2$  =  $65^\circ\text{C}$ ,  $\text{Pt}/\text{Al}_2\text{O}_3$  =  $95^\circ\text{C}$ ) was held while 70% of the reactant flow was diverted through a water bubbler at  $25^\circ\text{C}$  prior to delivery to the reactor, which resulted in  $\sim 2\%$   $\text{H}_2\text{O}$  in the reactant gas stream prior to the catalyst bed. The impact of water at a constant temperature was then monitored for at least 60 min or until the catalyst was stable. The catalyst was then cooled to ambient conditions and a  $30^\circ\text{C}$ – $150^\circ\text{C}$  temperature ramp was performed in humid reaction conditions (100 ppm  $\text{CO}$ , 2%  $\text{H}_2\text{O}$ , 20%  $\text{O}_2$ , 10% Ar and balance He).

Freon oxidation experiments were performed using a fresh catalyst (dry pretreatment) and exposing the catalyst to 10 ppm Freon 134a with  $\text{CO}$  oxidation reaction conditions (10 ppm Freon 134a, 100 ppm  $\text{CO}$ , 20%  $\text{O}_2$ , 20% Ar and balance He) at  $200^\circ\text{C}$  for 30 min, followed by a temperature ramp from  $200^\circ\text{C}$  to  $400^\circ\text{C}$ , holding for 30 min every  $25^\circ\text{C}$ . Freon 134a concentrations were calibrated and measured by online mass spectroscopy using  $m/z$  of 33 amu.  $\text{MeCl}$  oxidation experiments were performed identically to the Freon 134a oxidation experiments using 10 ppm  $\text{MeCl}$ , 100 ppm  $\text{CO}$ , 20%

$O_2$ , 20% Ar and balance He. MeCl partial pressures were calibrated and measured by online mass spectroscopy using  $m/z$  of 50 amu.

A catalyst stability test was performed on a fresh Pt/CeO<sub>2</sub> catalyst (15 mg, and diluted with silica gel, as stated above). The catalyst was pretreated as above, then exposed to CO oxidation reaction conditions, in addition to 2% H<sub>2</sub>O and 10 ppm MeCl at 30 °C. After ramping the catalyst to 50 °C, the catalyst was monitored for 48 h.

### 2.3. Catalyst characterization

#### 2.3.1. TEM

Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai12 TEM operating at 120 kV. Powdered catalysts were dispersed in deionized H<sub>2</sub>O and deposited on lacey carbon Cu grids (Ted Pella, Inc.). Pt particles appear darker in the TEM images than either Al<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> due to higher electron density. However, the contrast between Pt and Al<sub>2</sub>O<sub>3</sub> is more apparent due to the larger differences in atomic mass. Particle size distributions were determined by measuring at least 50 nanoparticle diameters for each material using ImageJ software.

#### 2.3.2. Diffuse reflectance fourier transform infrared spectroscopy

Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) measurements of CO chemisorbed on Pt catalysts were performed as described previously [28]. Briefly, each catalyst was loaded into a high temperature reaction chamber (Harrick Scientific), which was mounted inside a Thermo Scientific Nicolet iS10 FTIR spectrometer with a MCT detector and equipped with a Praying Mantis diffuse reflectance adapter (Harrick Scientific). All spectra were measured in Kubelka-Munk (KM) units by using a reduced catalyst as a background and averaging 128 scans at a resolution of 4 cm<sup>-1</sup>. Each catalyst was reduced as stated above (1 h at 230 °C in flowing H<sub>2</sub>), followed by flushing the cell out with He while cooling to ambient conditions. The catalysts were then exposed to saturation coverage of CO for 10 min, and spectra were taken 1 min after flushing the gas phase and physisorbed CO out of the reaction cell.

#### 2.3.3. Chemisorption & physisorption measurements

Support surface area measurements were performed by N<sub>2</sub> physisorption using a Micromeritics ASAP 2020 BET analyzer at -196 °C. Pt metal dispersions were measured via CO pulse chemisorption using a Micromeritics Autochem II 2920 gas analyzer. A typical procedure for measuring Pt dispersion involved loading ~500 mg of calcined catalyst into a U-shaped sample tube, and reduced at 230 °C for 1 h in 10% H<sub>2</sub>/Ar (Airgas). The catalyst was then flushed with He while ramping to 500 °C and holding for 30 min to degas the sample. After cooling to ambient conditions, pulse chemisorption measurements were performed with 10% CO/He (Airgas) and measuring the effluent using a thermal conductivity detector. Dispersion measurements were an average of 3 distinct measurements.

## 3. Results

### 3.1. Catalyst characterization and CO oxidation in a dry air stream

The dispersions of the two Pt catalysts determined from CO chemisorption were 23% ± 4% and 28% ± 11% and particle sizes determined from chemisorption measurements assuming a hemispherical particle were 5.0 ± 0.8 nm and 4.9 ± 2.1 nm for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> respectively. This is in reasonable agreement with the resulting particle size distributions from TEM analysis, which gave particle sizes of 6.4 ± 3.0 nm and 6.5 ± 1.6 nm for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>, respectively (Fig. 1). The relative similarity of the

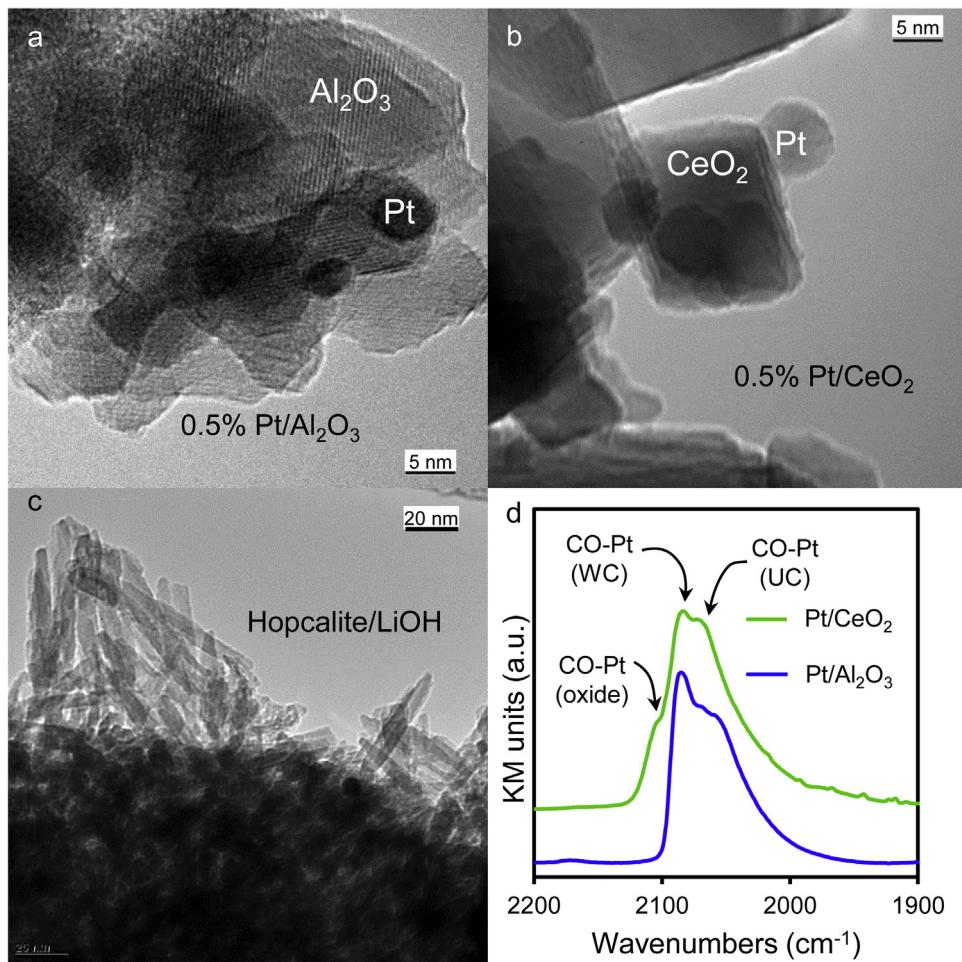
two Pt species was expected as both were synthesized as colloidal inks through identical approaches before deposition onto the supports. This was further confirmed by performing DRIFTS analysis of CO chemisorbed on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> catalysts (Fig. 1d). Both catalysts exhibit a similar distribution of CO bound to well-coordinated (WC) Pt and CO bound to under-coordinated (UC) Pt sites, as evidenced by the intensities of the peaks ~2085 cm<sup>-1</sup> and 2065–2070 cm<sup>-1</sup>, respectively [28]. In addition, the Pt/CeO<sub>2</sub> catalyst also had a small peak at a frequency of ~2105–2110 cm<sup>-1</sup> which is likely due to the partially oxidized interfacial sites at the Pt/CeO<sub>2</sub> interface [29,30]. The very similar characteristics the Pt nanostructures in the two catalysts allows us to assume that particle size effects on catalysis, comparing Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> is negligible, and any differences in the catalytic behavior of the two Pt catalysts is due to support effects [28]. The surface area of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> supports were 80 m<sup>2</sup>/g and 60 m<sup>2</sup>/g, compared to hopcalite/LiOH which was 220 m<sup>2</sup>/g (Fig. 1), consistent with previous reports [31,32].

Fig. 2 shows the influence of reaction temperature on CO conversion in a dry air stream and in the absence of any trace halogenated species over the three catalysts investigated in this report (100 ppm CO, 20% O<sub>2</sub>). All catalysts exhibited complete combustion of 100 ppm CO by 110 °C, with hopcalite/LiOH exhibiting the highest activity at low temperatures, followed by Pt/CeO<sub>2</sub> with complete CO removal by 80 °C and Pt/Al<sub>2</sub>O<sub>3</sub> showing the lowest activity with complete CO removal at <110 °C. Apparent activation barriers for Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> derived from low temperature CO oxidation data under differential conditions were found to be ~78 kJ/mol and ~59 kJ/mol for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>, respectively, which are consistent with previous reports [25,28,32]. Apparent activation barriers of CO oxidation on hopcalite barriers have been found to be somewhat lower than Pt based catalysts. Although differential reaction conditions could not be achieved above 30 °C in our study, our results are consistent with previous reports which show apparent activation barriers of ~45 kJ/mol for CO oxidation over CuMn<sub>2</sub>O<sub>4</sub> catalysts and has been attributed to a concerted spillover mechanism where Mn and Cu sites both act as active sites for O<sub>2</sub> and CO, respectively [33].

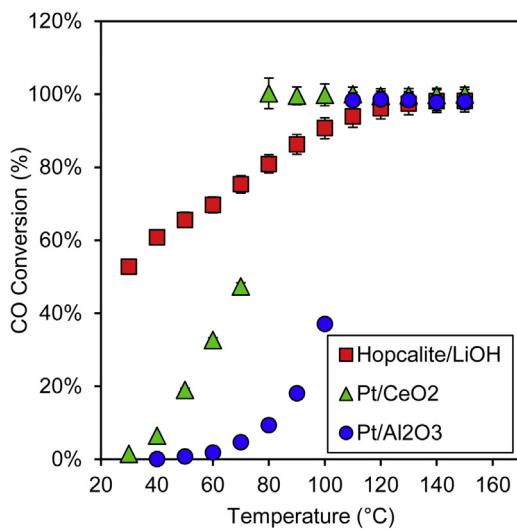
### 3.2. Influence of humidity on CO oxidation reactivity

In order to determine how each of the catalysts operated under humid environments that are typical of submarine atmospheres, isothermal experiments were performed where each catalyst was operated in a dry CO contaminated air stream at a temperature where 30–80% CO conversion was achieved. The catalysts were then exposed to ~2% H<sub>2</sub>O in the gas stream (~70% relative humidity at 25 °C, achieved by flowing 70% of the gas stream through a water bubbler) at constant temperature and reactivity was monitored over time. Fig. 3 shows the change in CO conversion as a function of time for the three catalysts. Hopcalite/LiOH exhibits a complete loss of activity to <5% CO conversion within 10 min, in agreement with previous results [12,13], whereas both Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> both exhibit a strong promotion of the CO oxidation reaction in upon exposure to 2% H<sub>2</sub>O. It should be noted that the initial spike in the CO conversion is due to changing partial pressures from switching the flow to the H<sub>2</sub>O bubbler.

After 6 h of flowing the reactants (100 ppm CO, 2% H<sub>2</sub>O, 20% O<sub>2</sub>) at constant temperatures, the catalysts were cooled and run at the same temperatures as the dry reactant stream (Fig. 2), while still under H<sub>2</sub>O flow (Fig. 4). The results show a large negative impact on the hopcalite/LiOH catalyst, where CO is not fully removed until temperatures >150 °C. The fast deactivation of hopcalite by humidity is well documented and has been attributed to H<sub>2</sub>O adsorption blocking O<sub>2</sub> activation sites and the change of Cu<sup>2+</sup> and Mn<sup>3+</sup> oxidation states [12,15]. In contrast, both Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> exhibit

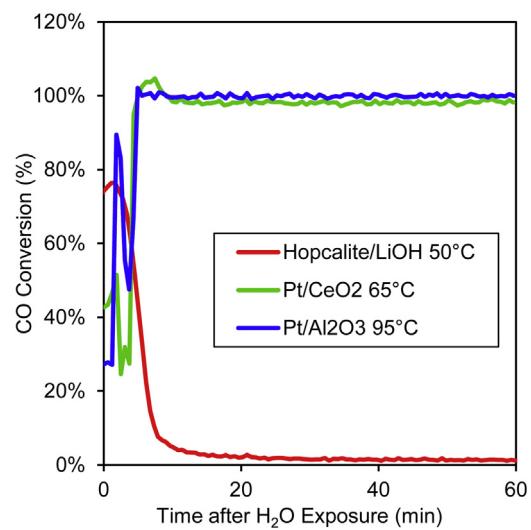


**Fig. 1.** TEM images of colloidally synthesized (a) 0.5% Pt/ $\text{Al}_2\text{O}_3$ , (b) 0.5% Pt/ $\text{CeO}_2$  and (c) a commercial hopcalite/LiOH catalyst. (d) DRIFTS spectra of CO chemisorbed on Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{CeO}_2$  catalysts at saturation coverage and room temperature.



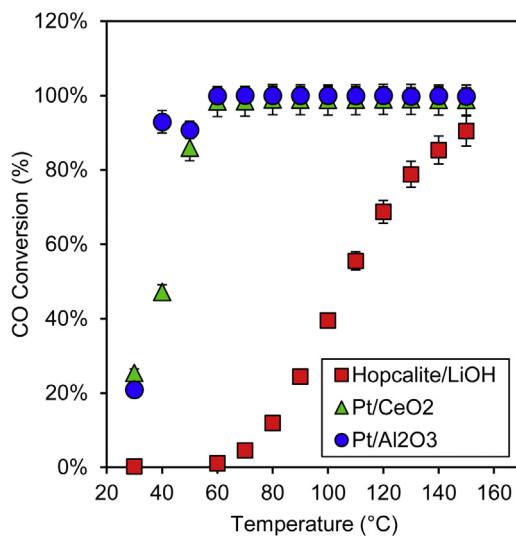
**Fig. 2.** Conversion of CO to  $\text{CO}_2$  by  $\text{O}_2$  as a function of temperature for Pt/ $\text{Al}_2\text{O}_3$ , Pt/ $\text{CeO}_2$ , and hopcalite/LiOH in dry CO oxidation reaction conditions (100 ppm CO, 20%  $\text{O}_2$ ).

higher CO conversions as a function of temperature, as compared to a dry stream, with complete CO conversion at similar temperatures (by 40 °C and 60 °C, respectively). This is consistent with reports in literature showing CO oxidation activities increase in the presence

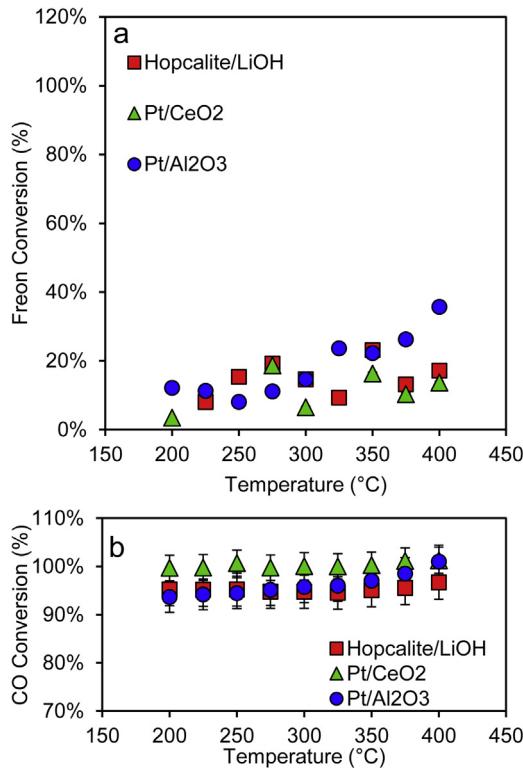


**Fig. 3.** Impact of water exposure on the CO oxidation activity of hopcalite/LiOH (50 °C), Pt/ $\text{CeO}_2$  (65 °C), and Pt/ $\text{Al}_2\text{O}_3$  (95 °C) in a stream of 100 ppm CO, 20%  $\text{O}_2$  and 2%  $\text{H}_2\text{O}$ . The initial spikes in CO conversion are due to changing  $\text{CO}_2$  partial pressures upon switching gas flow to the  $\text{H}_2\text{O}$  bubbler.

of water over Pt-based and three-way catalysts, and is most likely due to  $\text{H}_2\text{O}$  decreasing the binding strength of CO to the noble metal surface [20–24].



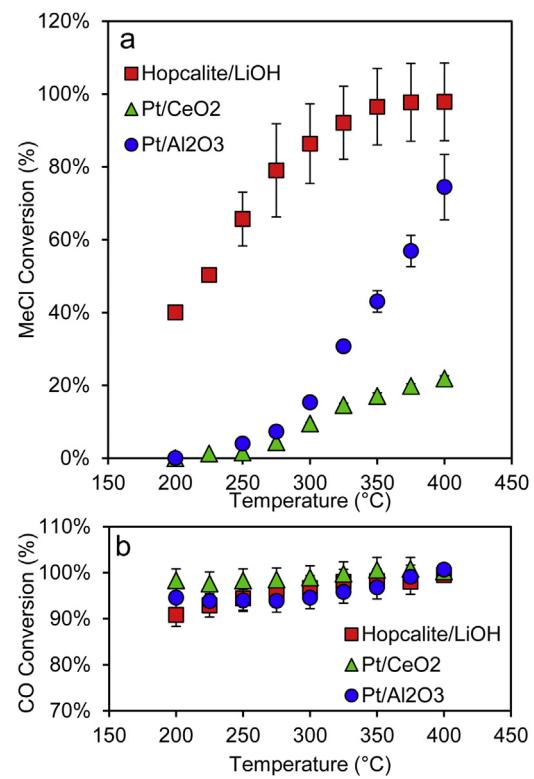
**Fig. 4.** CO conversion as a function of temperature for hopcalite/LiOH, Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> in a humid gas stream (100 ppm CO, 2% H<sub>2</sub>O, 20% O<sub>2</sub>) after operating for 6 h at conditions shown in Fig. 3.



**Fig. 5.** (a) Oxidation of Freon 134a over hopcalite/LiOH, Pt/CeO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in a stream of 10 ppm Freon 134a, 100 ppm CO, 20% O<sub>2</sub>. (b) Conversion of CO during freon oxidation experiment.

### 3.3. Catalytic oxidation of freon in a CO contaminated stream

The oxidation of 1,1,1,2 trifluoroethane (Freon 134a) as a model freon compound was investigated in a CO contaminated dry air stream over each catalyst at high temperatures (200–400 °C). Fig. 5 shows the impact of temperature on the consumption of freon in a gas stream consisting of 10 ppm Freon 134a, 100 ppm CO, 20% O<sub>2</sub>, 20% Ar and balance He. All catalysts exhibited minimal activation of freon in the temperature range studied, indicating that fluorinated hydrocarbons are fairly stable over the catalysts at these



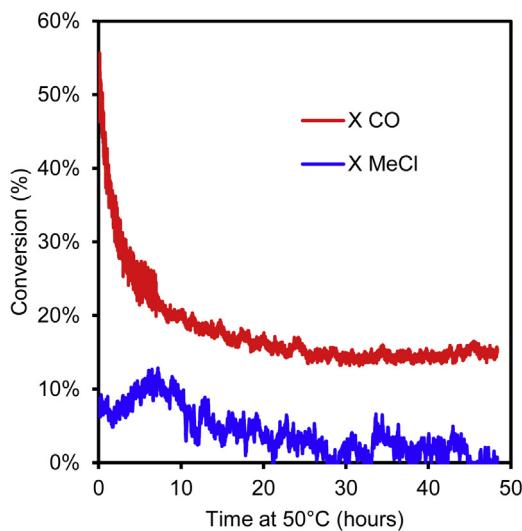
**Fig. 6.** (a) Oxidation of methyl chloride over hopcalite/LiOH, Pt/CeO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in a stream of 10 ppm methyl chloride, 100 ppm CO, 20% O<sub>2</sub>. (b) Conversion of CO during methyl chloride oxidation experiment.

temperatures, consistent with previous reports [34,35]. All catalysts exhibited 100% CO conversion at all temperatures (data not shown). These results show that freon oxidation is not a significant concern on any of the tested catalysts at reasonable operating conditions.

### 3.4. Catalytic oxidation of methyl chloride in a CO contaminated stream

Methyl chloride (also known as R-40) is a compound that has been widely used as a refrigerant, has been found in submarine atmospheres and is a model compound to investigate the cleavage of C–Cl bonds. Fig. 6 shows the conversion of MeCl as a function of temperature in a gas stream consisting of 10 ppm MeCl, 100 ppm CO, 20% O<sub>2</sub>, 20% Ar and balance He. It should be noted that we only measured the consumption of MeCl and did not attempt to identify which products were formed due to the trace amounts of products, but it has been shown that several harmful products can be produced, such as HCl, Cl<sub>2</sub>, and in some instances phosgene [36–38]. All catalysts also exhibited complete removal of CO at the temperatures investigated (200–400 °C, data not shown).

The MeCl consumption data shows at least 40% conversion of MeCl over the hopcalite/LiOH catalyst at 200 °C, which increases to ~100% by 350 °C. Chlorinated hydrocarbons have exhibited instability when passed over hopcalite based catalysts below 300 °C [35,38,39]. Both Pt based catalysts show no loss of MeCl below 275 °C, with Pt/Al<sub>2</sub>O<sub>3</sub> exhibiting higher activity at 400 °C (~80% conversion) than Pt/CeO<sub>2</sub> (~20% conversion). Chlorine is a well-known poison for Pt based catalysts, however it was observed here that MeCl was stable under reaction conditions at temperatures <275 °C, suggesting minimal interaction with the Pt surfaces [40–43].



**Fig. 7.** CO and methyl chloride oxidation activities during a 48 h stability test at 50 °C on the Pt/CeO<sub>2</sub> catalyst in a stream of 10 ppm methyl chloride, 100 ppm CO, 2% H<sub>2</sub>O, 20% O<sub>2</sub>.

### 3.5. Stability of Pt/CeO<sub>2</sub> in air contaminated with CO, MeCl and H<sub>2</sub>O

The stability of the Pt/CeO<sub>2</sub> catalyst was investigated by exposing the catalyst to 10 ppm MeCl, 100 ppm CO, 2% H<sub>2</sub>O in air, and monitoring the conversion as a function of time, while holding at 50 °C. Fig. 7 shows that the initial conversion of CO is ~50%, followed by a decay of the catalytic activity to ~15% over approximately 20 h, which remained stable for the subsequent 20 h on stream. In addition, the MeCl conversion indicates that MeCl reacts minimally during this experiment (never exceeding 10% conversion).

While it is apparent that deactivation of the Pt/CeO<sub>2</sub> catalyst occurred in the very initial time regime, the reactivity remained stable for an additional 20 h of analysis. We note that no efforts were made to reproduce much of the work that has been done in automotive catalysis to improve the stability of three-way catalysts in catalytic converters [44]. These approaches include washcoating catalysts onto honeycomb structured monoliths, including other thermally stable oxides, and using stabilizers such as barium and/or lanthanum oxides. It is expected that the catalytic performance and stability of the Pt-based catalysts can be further optimized by utilizing these approaches.

## 4. Discussion

### 4.1. Comparison of CO oxidation activity in dry stream

CO oxidation on irreducible oxide supported-Pt surfaces has been thoroughly studied, and has been shown to follow Langmuir Hinshelwood kinetics at low temperatures, where the surface is poisoned by CO, and the rate limiting step (RLS) is CO desorption to allow for CO-assisted O<sub>2</sub> activation [25,28,45]. In addition, the Pt-CeO<sub>2</sub> interface has been shown to enhance the rate of CO oxidation (as compared to Al<sub>2</sub>O<sub>3</sub> supported Pt), due to the reducibility of the CeO<sub>2</sub> support and participation of lattice oxygen [32]. However, the comparatively lower activation energies and reaction kinetics observed on hopcalite based catalysts at low temperatures has been related to a concerted spillover mechanism, where the RLS is related to CO chemisorption to Cu active sites, followed by the dissociation and spillover of adsorbed oxygen from the Mn site to the CO adsorbed on the Cu site [8,9,33]. In a dry stream free of trace halogenated compounds, all catalysts exhibit high activity

towards CO above 110 °C, where the activity trends in the order hopcalite/LiOH > Pt/CeO<sub>2</sub> > Pt/Al<sub>2</sub>O<sub>3</sub> below 110 °C.

### 4.2. Impact of H<sub>2</sub>O on CO oxidation rates

It has been proposed that the deactivation of copper and manganese mixed oxide catalysts in the presence of H<sub>2</sub>O is related to the change in surface concentration of the active phase Cu<sup>2+</sup>/Mn<sup>3+</sup> to Cu<sup>+</sup>/Mn<sup>4+</sup>, as determined by X-ray photoelectron spectroscopy (XPS) [12,13,15]. In addition, the blocking of active sites by H<sub>2</sub>O molecules [12] and phase segregation [15] have also been proposed to play roles in the deactivation of copper and manganese mixed oxides. In contrast, since CO oxidation over Pt-based catalysts at low temperatures (<80 °C) typically operate under CO poisoned conditions, any enhancements in rate can be attributed to an enhancement in the RLS, which is directly related to the Pt-CO binding energy [25,46]. Therefore, promotion of CO oxidation at low temperatures (<80 °C) in the presence of H<sub>2</sub>O has been attributed to the weakening of the CO-Pt binding energy [20–24]. In addition, the water gas shift reaction has been shown to play a minimal role at temperatures <200 °C, suggesting that H<sub>2</sub>O is not directly acting as a reactant under our reaction conditions [20]. These results highlight that Pt catalysts are much more robust than hopcalite/LiOH catalysts in potentially humid environments, due to the promotion of CO oxidation on Pt catalysts as compared to the strong deactivation of hopcalite/LiOH in the presence of H<sub>2</sub>O. Operationally this would mean that Pt based catalysts could be operated at lower temperatures in CO burners, yielding higher efficiency of the pollution control unit, likely also resulting in longer lifetimes for the catalysts.

### 4.3. Discussion of MeCl activity

Hopcalite catalysts have been shown to be active for the destruction of several chlorinated compounds in the temperature range of 250 °C–350 °C, including the decomposition of methyl chloroform, vinylidene chloride, trichloroethylene, and tetrachloroethylene to primarily hydrochloric acid [38,39]. To combat the production of these dangerous compounds, up to 10% LiOH has been added to the hopcalite catalyst beds to act as a sorbent to reduce and neutralize the acid gases in the exhaust stream [4,38]. We found no observable differences between hopcalite/LiOH and Carulite 300 (hopcalite with no LiOH added) during low temperature (30 °C–150 °C) CO oxidation experiments in a dry stream or for high temperature (200 °C–400 °C) MeCl consumption activity (data not shown). LiOH is likely acting as a sorbent for acid gases produced during MeCl consumption while having little to no impact for adsorbing MeCl, hence the reason we see no difference between the hopcalite materials for MeCl consumption. Just as a reminder, we only monitored the consumption of MeCl and not the formation of products for this particular reaction.

The impact of chlorine on the catalytic activity of Pt catalysts has been widely studied and is known to exhibit poisoning of the Pt catalyst by chlorine [40–43]. Interestingly, we observed that the Pt/CeO<sub>2</sub> catalyst was less reactive towards MeCl conversion as compared to Pt/Al<sub>2</sub>O<sub>3</sub> and much less reactive than hopcalite/LiOH. Due to the similar Pt size and structure in the CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported catalysts it is suggested that a support effect renders Pt/CeO<sub>2</sub> less reactive than Pt/Al<sub>2</sub>O<sub>3</sub> for activation of C–Cl bonds in CO contaminated environments, as this is likely the RLS for MeCl combustion [47]. We hypothesize that the Pt-Cl bond (Cl is highly electronegative) on the Pt/CeO<sub>2</sub> catalyst (which exhibits δ<sup>+</sup> charged interfacial Pt atoms after charge donation to the CeO<sub>2</sub> support caused by Pt-O bond formation; see Fig. 1d) is weaker than on the more neutral Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [29,30,48]. The weaker Pt-Cl interaction on the Pt/CeO<sub>2</sub> system would be expected to result in a higher barrier

for C–Cl bond activation on the Pt surface, due to the well-known Bronsted–Evans–Polanyi relation, and thus lower reactivity. The slightly higher activity of Pt/Al<sub>2</sub>O<sub>3</sub> is also consistent with recent results of hydrodechlorination of trichloroethylene over Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, which also showed a higher conversion of trichloroethylene over Pt/Al<sub>2</sub>O<sub>3</sub>, as compared to Pt/CeO<sub>2</sub> [47]. The results of Fig. 6 clearly show that hopcalite/LiOH catalysts exhibit a much higher tendency towards the destruction of C–Cl bonds than Pt catalysts at short time scales in CO contaminated air, at temperatures >200 °C. Fig. 7 shows that reactivity of the Pt/CeO<sub>2</sub> catalyst deactivates over a short initial period, but then stabilizes on longer time scales. No attempt was made to optimize this catalyst for stability. It has been clearly demonstrated that Pt and other precious metal catalysts can perform remarkably well over long periods of time (years), and under harsher conditions in catalytic converters [18,44].

## 5. Conclusions

In a comparison of hopcalite/LiOH and Pt based catalysts, CO oxidation activity in a dry air stream contaminated with 100 ppm CO, was observed to be slightly different at low temperatures, with hopcalite/LiOH being the most active, followed by Pt/CeO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub>. All catalysts exhibit complete CO removal by 110 °C. A complete deactivation of the hopcalite/LiOH catalyst and promotion of CO oxidation over Pt/CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts in the presence of 2% H<sub>2</sub>O indicate that Pt based catalysts are more robust and are more active for CO removal at temperatures below 60 °C in humid environments, which are typically found onboard submarines. All catalysts exhibited minimal activity towards oxidation of the model fluorinated hydrocarbon, freon 134a, indicating that C–F bonds are relatively stable under the explored conditions. However, hopcalite/LiOH exhibited high activity towards cleaving C–Cl bonds in MeCl at temperatures as low as 200 °C, whereas both Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> exhibited a small amount of activity above 275 °C. Pt/CeO<sub>2</sub> uniquely exhibited high CO oxidation reactivity and the lowest MeCl oxidation reactivity.

In the context of the ideal catalyst characteristics for naval submarine pollution control, Pt based catalysts showed clear beneficial behaviors as compared to currently used hopcalite/LiOH catalysts. Notably, Pt-based catalysts were shown to be more robust in the presence of humidity and have a lower activity towards breaking C–Cl bonds into potentially dangerous and toxic compounds. Currently used hopcalite/LiOH catalysts require increased operating temperatures over time in order to combat deactivation by H<sub>2</sub>O, which in turn increases operating costs, as well as increases the amount of potentially dangerous and toxic compounds formed from the decomposition of chlorinated refrigerant molecules. In addition, Pt catalysts are more active per gram of active material, and have been shown to be stable for years under harsher conditions in automotive catalysis, indicating that the operating and maintenance costs of Pt-based catalysts may be more appealing than hopcalite/LiOH. Pt-based catalysts exhibit behavior that combats negative chemical and economic characteristics of hopcalite/LiOH and thus, Pt based catalysts would provide significant advantages over hopcalite catalysts for confined space pollution control applications.

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